

The University of Chicago

A STUDY OF THE ABSORPTION
SPECTRA OF SULFIDES, THIOSULFATES AND
THIONATES WITH REFERENCE TO
STRUCTURAL RELATIONSHIPS

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1933

By

VERNE DONALDSON SNYDER

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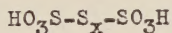
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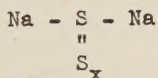
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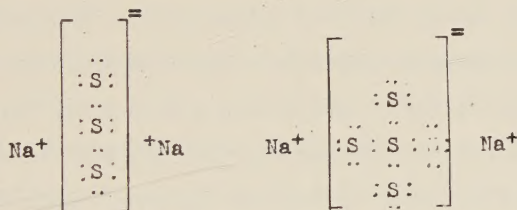
Since the discovery of the polythionic acids there has been much speculation concerning their structure. In general, two types of hypotheses have been advanced; in the one the sulfur atoms are thought of as linked in straight chains of varying lengths, as might be represented by the formula



in which x may vary from zero to four; and in the other the binding of the sulfur atoms is assumed to be similar to that existing in the polysulfides, which is assumed to be



in which x may vary from one to five. According to the Lewis theory there can be only one form of structure for the lower polysulfides, with a possible variant for the higher members of the series:



As sulfur is added to an alkali sulfide the change in absorption spectrum is gradual. The pentasulfide is the simplest polysulfide which could have one sulfur atom completely surrounded by sulfur atoms and sharing all of its electrons with other sulfur atoms. There is no spectroscopic evidence to indicate that the pentasulfide is essentially structurally different from the lower polysulfides. This indicates that the two polythionate structures mentioned above, have much in common. Although polysulfides are

highly colored, whereas polythionates are colorless, very little weight has been attached to this fact, and the polysulfide structure is still favored by such writers as Raschig,¹ Ephraim,² Vogel,³ etc. It was thought that a more detailed study of the colors, i.e., of the absorption spectra of solutions of these and related substances, might lead to the discovery of important relationships between them.

This investigation has brought out the fact that none of these substances displays specific absorption; and absorption was observed in all cases, and except for the solutions of sulfur in various solvents, and of the polysulfides, the end absorption is in the far ultraviolet. In the absence of specific absorption it is very difficult to establish structural relationships by this method, and we shall, therefore, content ourselves with a report of the experimental results, and a very brief discussion of their theoretical bearing.

The most striking observations are these. Solutions of the alkali metal salts of thiosulfuric, trithionic, and tetrathionic acids produce absorption spectra practically identical with those obtained with sodium hydrogen sulfide (or with solutions of sodium sulfide containing too little alkali completely to prevent hydrolysis). These absorption spectra, furthermore, are very similar to those of liquid hydrogen sulfide. They are, however, decidedly different from those obtained with sodium sulfite and with sodium dithionate, on the one hand, and from those obtained with polysulfides and with solutions of sulfur in various solvents, on the other hand.

¹Raschig, Schwefel und Stickstoffstudien.

²Ephraim, Anorganische Chemie.

³Vogel, J. Chem. Soc. (London) 127, 2248 (1925).

From these results one may draw a number of conclusions of general character. Dithionic acid behaves spectroscopically as the mixed anhydride of sulfuric and sulfurous acids, and is in no way related to the other polythionates. This is in full agreement with its chemical behavior, and there is no justification for classifying dithionates with the other polythionates, or for basing structural formulae for others on that of the dithionate. According to the spectroscopic data obtained thiosulfuric, trithionic and tetrathionic acids contain the same actinic group, which is also present in liquid hydrogen sulfide and in acid sulfides. Neither the dithionates nor the group in which thiosulfates and the polythionates have thus been classified displays absorption similar to that of the polysulfides, and it therefore seems unjustified to give these substances a polysulfide structure.

Experimental

The substances of which the absorption spectra were to be studied are particularly liable to contamination by each other. Furthermore, the absorption was found in most cases to lie so far in the ultraviolet that small amounts of impurity might on that account introduce enormous errors. For this reason particular attention was paid to the purification of the materials. The various salts were prepared according to methods described below, and the thiosulfate and the polythionates were purified according to the following general scheme. The salt was dissolved in the minimum quantity of water at room temperature, and the water so slowly evaporated in a crystallizing dish in a vacuum desiccator over a suitable dehydrating agent, sometimes sodium sulfate, sometimes phosphoric anhydride, that the crystals which were formed were large enough to be picked out with forceps. In this way the characteristic crystals were selected, and the recrystallization con-

tinued until there was no change in the absorption spectrum in the last crystallization. In the case of the trithionate a quartz dish was used to reduce the decomposition of the salt. These recrystallizations were extended over a period of two years.

Because of the fact that the sulfur content of the thiosulfate and the various polythionates does not differ greatly, and these are the substances which would contaminate each other, analytical methods are not accurate enough as a criterion of purity. Consequently the spectra themselves have been used for this purpose.

The sodium dithionate was prepared by passing sulfur dioxide into a suspension of fifty grams of powdered manganese dioxide and 250 cc. of water; during this time the mixture was cooled with tap water. After two and a half hours the mixture was diluted to one and one-half liters, heated to boiling, and a hot solution of two hundred grams of barium hydroxide was added. After separating the solid manganese hydroxide and barium sulfate from the solution and precipitating the excess of barium hydroxide in the usual way, the solution was evaporated to half its volume, filtered while hot, and the barium dithionate allowed to crystallize. These crystals were dissolved in water, and the required quantity of a solution of sodium sulfate was added. The barium sulfate was removed by filtration and the solution evaporated slowly in a vacuum desiccator to obtain crystals of sodium dithionate.

Potassium trithionate was obtained by passing sulfur dioxide into a saturated aqueous solution of potassium thiosulfate. The potassium trithionate soon crystallized and was recrystallized from lukewarm water.

Sodium tetrathionate was prepared by triturating fifty grams of sodium thiosulfate, twenty-six grams of iodine, and five grams of water to a bright brownish paste. This was rinsed into

an Ehrlenmeyer flask with forty grams of alcohol. After three hours the precipitated sodium tetrathionate was drained and washed with alcohol to remove the last trace of iodine. The crude product was dissolved in twenty-five grams of lukewarm water. Forty grams of alcohol were added, and the mixture allowed to stand in a vacuum desiccator for ten hours. The crystals were then drained, washed with alcohol, and dried in a desiccator over sulfuric acid.

The hydrogen sulfide used in these experiments was prepared from arsenious sulfide and hydrochloric acid. The gas was passed through water to free it from hydrogen chloride, partially dried by passing it through a spiral glass tube surrounded by liquid ammonia at reduced pressure, and further dried by passing it over phosphoric anhydride.

Hydrogen polysulfides were prepared according to the method described by Walton and Parsons.¹ Essentially the same conditions of purification were used, except that lower pressures and temperatures were employed. The distillation was performed in all-quartz apparatus, and the heating was done on an oil bath. The first receiver was cooled by ice, and the second receiver was cooled by liquid ammonia at reduced pressure. The reduced pressure for distillation was maintained by a two stage Geyrk pump, protected by a drying tower filled with soda lime. Repeated distillations of the crude materials separated them into three components, sulfur, hydrogen sulfide, and a clear yellow liquid, analysis of which indicated the composition of hydrogen disulfide.²

¹Walton and Parsons, J. Am. Chem. Soc. 45, 2539 (1921). See also Bloch and Hohn, Ber. 41, 1961 (1908).

²Bloch and Hohn, as well as Walton and Parsons assume the existence of hydrogen trisulfide, which has a percentage composition in close agreement with that of the liquid collected by them in their first receiver. According to our results this composition is variable, depending on the temperature of condensation. The lower the temperature the greater is the solubility of hydrogen

The sodium sulfide used was obtained in two ways. A 5·N solution of sodium hydroxide was divided into two parts, one of which was saturated with hydrogen sulfide, and then added to the other, thus making an approximately 5·N solution of sodium sulfide. This was diluted for use as desired. The spectra of these solutions were checked with the spectra of solutions made with Mallinckrodt's best grade of sodium sulfide. Sodium sulfite was similarly prepared.

The carbon bisulfide used as a solvent for determining the absorption spectra of sulfur was purified by distillation, then shaken with mercury, and again distilled. After this treatment, the material had been purified to the extent that it had a very slight, pleasant odor; purification had, however, not shifted the position of end absorption which was so near the visible that the solvent was not suitable for work with sulfides of hydrogen. However, it was employed to obtain the spectra of solutions of sulfur.

Carbon tetrachloride, to be used as a solvent, was purified by treatment with chlorine in sunlight, and in the light from a pyrex mercury vapor lamp, with subsequent distillation, drying and redistillation. This treatment accomplished only a slight shift in the position of end absorption, and that shift is due to the re-

sulfide in the disulfide, and the lower the sulfur content in the material in the first receiver. Undoubtedly the pressure at which distillation is performed also influences the composition, but our experiments were always carried out at the lowest possible pressure (about 2 mm.), and we can make no definite statement about the pressure effect. Since the solution of hydrogen sulfide in hydrogen disulfide readily dissolves sulfur, which is produced by the decomposition of the disulfide, it would seem that the existence of the trisulfide should receive further verification. Our own experiments were not directed toward the solution of this problem.

The decomposition of hydrogen disulfide liberates sulfur, which is soluble in the mixture and imparts a dark reddish color to it. Ultimately only sulfur is left. This decomposition is hastened by contact with glass, and for this reason quartz tubes and flasks were used.

moval of water.¹

These absorption spectra were determined with a Hilger quartz spectrograph and sector photometer. Illumination was obtained by a Tesla discharge under water, in a tube developed for this work, and previously described.²

Liquid hydrogen sulfide at ordinary temperatures has a vapor pressure in the neighborhood of twenty-five atmospheres. Obviously the spectra of the liquid and of solutions in this solvent cannot be obtained with the usual apparatus. Instead, the special cell, shown in Figure 1, was designed. It consists of a brass shell carrying two quartz windows, a, a, and a small brass sleeve, b, closely fitting the quartz tube, c. The brass sleeve, b, is held in position by two brass strips, d, d, which also serve as light shields. The quartz tube, c, is held in position by two rubber stoppers, one at the top, and one at the bottom of the brass shell. The brass sleeve, b, has two narrow slits so arranged as to permit light to pass through only the middle portion of the quartz tube, c. The large brass shell is filled with water in order that there shall be little refraction as the light passes through the quartz tube and the solution which it contains.³

¹The absorption spectra of sulfur and of sulfides of hydrogen dissolved in this solvent were identical in dilute solution with the spectra of these substances dissolved in liquid hydrogen sulfide, and in carbon bisulfide in concentrated solutions a dark yellow color, not observed in the other solvents, appears.

²Snyder, J. Am. Chem. Soc., 49, 2510 (1927).

³In these experiments with liquids and vapors under high pressure, the tubes were handled only when at least one part of the quartz tube was surrounded by liquid ammonia. At other times the operator was protected by two pieces of half inch plate glass, with wire reinforcing. All of the tubes, except those containing hydrogen disulfide, were tested by placing them in water at fifty degrees, Centigrade, before placing them in front of the slit of the spectrograph. In the whole series of experiments only one tube failed to withstand the pressure, and that one broke while in the hot water test. The method is not particularly dangerous.

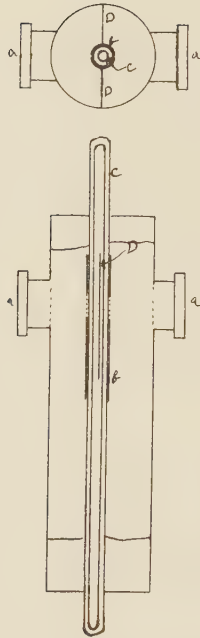


FIG. 1

With this apparatus the extinction coefficients were determined as follows. A photograph was obtained by allowing the light from the lamp, mentioned above, to pass through a quartz condensing lens and the solution in the quartz tube for a measured period of time, thus producing a photograph of a certain intensity. Next, the plate holder of the spectrograph was moved sufficiently to leave a gap between the first photograph and the second one, which was obtained in the same way, but with a different length of exposure. The process was repeated with a number of different exposures. After this series had been obtained the spectrum of the solvent itself was photographed on the gaps between the photographs of the spectra of the solution; the time of exposure used in obtaining the spectrum of the solvent was in every case the same as the time of exposure for the first photograph of the solution. These photographs of the spectra of the solution can then be compared with those of the solvent to find the wave length at which the intensities are equal, just as is done when a sector photometer is employed. In order that these photographs may be used for calculating extinction coefficients it is necessary that they be made with a light source of constant intensity, since the exposures for solution and solvent are not simultaneous, as they are in the usual methods for measuring intensities.

It was assumed that if the current through the lamp was kept constant, as measured by a hot wire ammeter, the intensity of the light would also be constant. The correctness of this assumption was tested by obtaining the spectrum of potassium nitrite in this way, and showing it to be identical with that obtained with the sector photometer.

The data are presented in three tables and sixteen graphs. The sector graduations, and wave lengths at which the two beams are

of equal intensity, are recorded in the tables. The sector graduations are numerically equal to the logarithm of the ratio of the intensity of the incident light to the intensity of the emergent light. In the graphical presentation of the data, the wave lengths and molecular extinction coefficients are used as coordinates. The molecular extinction coefficient is given by

$$\text{M.E.C.} = \frac{\log \frac{I_0}{I}}{C D}$$

where I_0 is incident intensity, and I is emergent intensity, D is the length of absorbing column, and C is the molar concentration, except that in the case of sulfur in hydrogen sulfide, the molecular weight of sulfur is not known, and in this case the atomic concentration of sulfur is used.

A comparison of graphs Nos. 7, 8, and 9 shows the manner in which sodium thiosulfate follows Beer's Law. With the other materials the deviation is wide, probably due to hydrolysis. This deviation is not recorded here because it is not within the scope of this work.

A comparison of graphs Nos. 4 and 6 shows the effect of hydrolysis on sodium sulfide, for in a water solution of hydrogen sulfide there is little sulfide ion.

A comparison of graphs Nos. 3 and 4 shows the effect of a large excess of sodium hydroxide on the spectrum of sodium sulfide solutions. The observations were made to determine whether sulfide ion and acid sulfide ion are different in optical properties. It was expected that, at most, a very slight difference would be observed in view of the fact that normal and acid salts, in cases where tautomerism is excluded, usually have very similar spectra. The very large shift, in the spectrum resulting when a large excess of sodium hydroxide is added to sodium sulfide was, therefore, en-

tirely unexpected. Since this shift is toward the visible, i.e., in the direction which would result from the formation of polysulfides as a result of oxidation of the solutions, a second set of observations was made with solutions from which oxygen was as completely excluded as possible. Hydrogen, most carefully freed from oxygen, was passed through the heated water for from two to ten hours before the sodium sulfide was added, and the solution was prepared and observed in an atmosphere of hydrogen. The sodium hydroxide was diactinic. All of these precautions did not alter the spectrum; nevertheless, since no other adequate explanation of the phenomenon seems reasonable, we are not yet ready to conclude that residual traces of oxygen may not have produced the observed effect.

The absorption spectra of liquid hydrogen sulfide was obtained merely because the substance was used as a solvent in several of the experiments.

Summary

The absorption spectra of hydrogen disulfide, hydrogen sulfide, sodium sulfide, sodium thiosulfate, potassium trithionate, sodium tetrathionate, and sodium dithionate have been quantitatively determined in comparable solutions. It is shown that the sulfide, thiosulfate, trithionate and tetrathionate are spectroscopically related as to structure, and that they are not related to the dithionates, on the one hand, nor are they related to the polysulfides, on the other hand.

This work was carried out with the aid of a grant from the Bache fund of the National Academy of Sciences.

In conclusion, I want to express my gratitude to Professor Schlesinger, and my appreciation of his advice and counsel. His friendly interest and direction have made this work possible.

- Solution No. 1. 1.325 molar hydrogen disulphide in liquid hydrogen sulphide in a three millimeter cell.
2. 0.476 gram atoms of sulphur in liquid hydrogen sulphide in a three millimeter cell.
3. 0.05 molar sodium sulphide and 10 molar sodium hydroxide in aqueous solution in a 1 cm. cell.
4. 0.125 molar sodium sulphide and 0.125 molar sodium hydroxide in aqueous solution in a 1 cm. cell.
5. Hydrogen sulphide liquid, 26.4 molar, in a three millimeter cell.
6. 0.195 molar hydrogen sulphide aqueous solution in a one centimeter cell.
7. 0.1 molar sodium thiosulphate aqueous solution in a one centimeter cell.
8. 0.01 molar sodium thiosulphate aqueous solution in a one centimeter cell.
9. 0.05 molar sodium thiosulphate aqueous solution in a two centimeter cell.
10. 0.1 molar sodium thiosulphate and molar sodium hydroxide aqueous solution in a 1 cm. cell.
11. 0.1 molar potassium trithionate aqueous solution in a one centimeter cell.
12. 0.1 molar potassium trithionate and 0.5 molar potassium hydroxide aqueous solution in a 1 cm. cell.
13. 0.05 molar sodium tetrathionate aqueous solution in a one centimeter cell.
14. 0.01 molar sodium bisulphite aqueous solution in a one centimeter cell.
15. 0.1 molar sodium dithionate aqueous solution in a one centimeter cell.

Absorption spectra of sodium bisulphite. No. 14.

λ	3060	3010	2945	2915	2840	2740	2700	2637	2540	2500
θ	0.0	0.1	0.2	0.3	0.4	0.4	0.3	0.2	0.1	0.2

Sector photometer scale reading															
Wave lengths															
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4 1.5
1	4125	4100	4060	4050	4025	4010	4000	3990	3980	3975	3970	3965	3960	3950	--
2	3700	3630	3580	3565	3550	3535	3528	3518	3510	3490	3488	3486	3484	3480	3475 3470
3	4260	3530	3167	3070	3030	2990	2972	2960	2938	2930	2920	2910	2902	2896	2894 2892
4	3098	2986	2897	2832	2811	2790	2770	2760	2757	2753	2748	2744	2740	2738	2736 2732
5	2780	2757	2730	2713	2708	2700	2694	2688	2677	2670	2668	2664	2660	2658	2654 2650
6	--	2765	2615	2550	2495	2475	2452	2435	2427	2418	2411	2405	2395	2388	2382 2370
7	3100	2949	2871	2838	2809	2787	2778	2770	2760	2749	2735	2730	2728	2722	2717 2710
8	2857	2718	2688	2674	2659	2644	2627	2619	2611	2607	2598	2593	2590	2582	2577 2570
9	3036	2879	2840	2810	2793	2775	2764	2750	2742	2738	2731	2722	2715	2710	2708 2704
10	3100	2976	2920	2885	2864	2857	2848	2840	2830	2820	2812	2808	2800	2798	2796 --
11	3100	2905	2855	2825	2800	2783	2775	2760	2753	2745	2738	2728	--	--	--
12	3085	2950	2905	2886	2855	2822	2800	2785	2767	2748	2738	2728	--	--	-- 2694
13	3000	2868	2812	2783	2758	2730	2716	2680	2653	2627	2605	2587	2558	2539	-- 2527
15	--	2256	2231	2217	2205	2200	--	--	--	--	--	--	--	--	--

Solution numbers

